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**THEORY AND DESIGN CONSIDERATIONS
IN DEVELOPING A MULTI-PURPOSE
INSTRUMENT FOR DETERMINATION OF
TWELVE PROPERTIES**

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A MULTI-PURPOSE INSTRUMENT FOR PRECISE
DETERMINATION OF 12 PROPERTIES AT
TEMPERATURES FROM - 190°C TO 650°C AND
AT PRESSURES FROM VACUUM TO 500 ATM*

A. General Theory and Design Considerations
in Extending Capability of a Thermal
Conductivity Cell to That of a
Multi-Purpose Instrument**

by
W. Leidenfrost ***

* The paper was presented at Physikalisch Technische Bundesanstalt Braunschweig, Germany in January 1966, at VDI meeting Hochdruck-Verfahrenstechnik in Baden-Baden, March 1966 and also at the 6th Thermal Conductivity Conference at Dayton, Ohio

** Successive papers will describe in detail the design of the major parts of the multi-purpose instrument and experimental results obtained.

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ABSTRACT

The development of a new instrument is described and also techniques of measurement to determine; for fluids: 1) thermal conductivity, 2) dielectric constant, and hence 3) index of refraction, 4) electrical conductivity a.c., 5) electrical conductivity d.c.; for gases and vapors: 6) p-v-T properties; for liquids: 7) thermal expansion coefficient, 8) compressibility, 9) vapor pressure, 10) specific heat c_p , 11) specific heat c_v ; for solids: 12) specific heat; and for instrument materials; thermal expansion coefficient and Young's modulus. A new thermostat operating from about -190°C to $+650^{\circ}\text{C}$ is described. This device is controlled automatically and can follow preset temperature-time functions. Detailed analysis is made for the procedure necessary to establish isothermal conditions at surfaces wetted by the test substances and to evaluate deviations from such conditions due to the disturbance of the temperature field in the neighborhood of the surfaces caused by the temperature sensing elements. This also is important so that the correct surface temperature can be derived from the readings of the thermometer. The construction of the centering rod (the most critical part of the multipurpose instrument being a double electrically shielded lead-in and a centering device) is described as is also briefly the final design of the apparatus.

ZUSAMMENFASSUNG

Die Entwicklung eines neuen Instrumentes und die Technik der Messungen werden beschrieben für die Bestimmung von Stoffgrössen von flüssigen Medien: 1) Wärmeleitzahl, 2) Dielektrizitäts-Konstante und damit, 3) Brechzahl, 4) elektrische Leitfähigkeit (Wechselstrom), 5) elektrische Leitfähigkeit (Gleichstrom); von Gasen und Dämpfen: 6) p-v-T Zustandsgrössen; von Flüssigkeiten 7) thermischer Ausdehnungskoeffizient, 8) Kompressibilität, 9) Dampfdruck, 10) spezifische Wärme c_p , 11) spezifische Wärme c_v ; und von festen Körpern: 12) spezifische Wärme und Wärmeausdehnungskoeffizient und Elastizitätsmodul des Instrumentmaterials. Ein neuer Thermostat der in einem Temperaturbereich von -190°C bis $+650^{\circ}\text{C}$ arbeitet wird beschrieben. Dieses Instrument wird automatisch geregelt und kann vorbestimmten Temperatur-Zeit-Funktionen folgen. Die notwendigen Schritte um isotherme Verhältnisse an den, von der Versuchssubstanz benetzten Wandungen, zu erreichen, werden analysiert. Ebenfalls die Abweichungen vom isothermen Verhalten infolge der Störungen des Temperaturfeldes durch die eingebauten Temperaturfühler. Was auch wichtig ist für die Ermittlung des Temperaturabfallen in der Wand um die wahre Oberflächen-Temperatur zu erhalten. Der kritischste Teil der Apparatur ist die Zentrierung die gleichzeitig als doppelt elektrisch abgeschirmte Zuleitung dient. Die Konstruktion dieses Zentrierhalses ist im einzelnen beschrieben und kurz nur der endgültige Entwurf des gesamten Mehrzweckmessgerätes.

NOMENCLATURE

A	average cross-sectional area of test fluid in gap between hot and cold body
A_r	surface area of calorimeter heater
a	thermal diffusivity of sample
B	geometric constant
b	wall thickness of instrument
C	electrical capacitance of the cell assembly
c	specific heat
c_v	specific heat at constant volume
c_p	specific heat at constant pressure
D	dielectric loss of test fluid
I	electric current through heater of hot body
ΔI	error in current measurements
i	electric current through test material
k	thermal conductivity of test material
k_h	apparent thermal conductivity of thermometer placed in a hole
k_w	thermal conductivity of material of instrument
k_{Au}	thermal conductivity of gold
L	thickness of layer of test fluid also used for half-wavelength of locally periodic temperature distribution
l	thickness of wall between surface and location of thermometer, thermometer perfectly centered and uniform heat contact
l_1, l_2	thickness of wall between surface and location of thermometer, thermometer not perfectly centered and no uniform heat contact.

m	mass of test sample
n	index of refraction
ΔP	electrical potential difference between hot and cold body
p	pressure
q	continuous power input into heater of calorimeter
q_c	heat flow by free convection
q_{inh}	increase of heat flow due to inhomogeneities in temperature field
q_k	heat flow by conduction through layer of test fluid and walls of instrument
q_L	heat loss from hot body along centering rod
q_{osc}	heat losses or gains due to unsteady state conditions
q_r	heat flow by radiation
R	outer radius of calorimeter, also used for electrical resistance of test fluid
r	outer radius of calorimeter heater
T	temperature
t	time
T_{cold}	surface temperature of cold body
T_{hot}	surface temperature of hot body
T_o	initial temperature of instrument
T_m	amplitude of temperature fluctuation
\dot{T}	temperature change in time
V	electrical potential
ΔV	error in potential measurements

v	specific volume of test material
w	width of nonisothermal area
w_c	heat capacity of calorimeter body
x	coordinate
y	coordinate

Greek symbols

β	thermal expansion coefficient of test substance
ϵ	dielectric constant of substance
ϵ_g	dielectric constant of gas
ϵ_v	capacitance of vacuum
κ	compressibility coefficient
λ	electrical conductivity
$\lambda_{a.c.}$	electrical conductivity (a.c.)
$\lambda_{d.c.}$	electrical conductivity (d.c.)
τ	dimensionless time
τ_b	dimensionless time when steady state conditions are achieved
θ	dimensionless temperature
ω	frequency
ζ	dimensionless coordinate
ξ	dimensionless coordinate

INTRODUCTION

A knowledge of the properties of materials over wide ranges of pressure and temperature is essential to present-day technology. To determine all properties of all materials is a never ending and practically hopeless task because new materials are constantly developed, and furthermore, data are sometimes needed under conditions where it is impossible to carry out measurements.

In addition to the needs of the engineer, a scientist who tries to predict property values by statistical mechanics requires basic information in the form of accurate property values to verify and check his models. The more information, i.e., the more data of different properties of importance to theory, he obtains and the wider the range of pressure and temperature in which those values have been observed, the more successful his theoretical treatment becomes and the reliability of calculated data increases even for conditions where measurements are as yet impossible. All the facts make it understandable that in the last decades a large and constantly increasing effort has been spent in expanding our knowledge of properties of materials. The results obtained so far are behind expectation for many reasons. One of them is that different properties of the same material or properties of different materials measured normally are not observed under identical conditions of pressure and temperature. This is also true when the same property has been investigated in different apparatus. The situation is worsened by the fact that tests in different apparatus of a supposedly same material have not necessarily been carried out with material that is, in fact, identical. Impurities might not have been the same to begin with and furthermore the material might have changed differently during the various tests. Intercomparisons are therefore very difficult to make.

These difficulties accompanying property research can be lessened or avoided by using multi-purpose instruments able to determine simultaneously several properties in one and the same instrument under identical conditions of pressure, temperature and impurity content, and over ranges of pressure and temperature which are as wide as possible but feasible for precise measurements. Simultaneous determinations of more than one property can improve in addition the precision of the investigation because one observed property might be needed for the correction of another one measured in the instrument under identical conditions.

The use of multi-purpose instruments promises also to be of advantage in the field of biology. Property determinations of organic material might be a tool to study macromolecules and to detect most of all the changes of their qualities under the influence of varying environment conditions.

Multi-purpose instruments applied for property research will also reduce costs, time and manpower since only one instrument, one instrumental setup and one group of people are needed for the measurements of several properties. For the observations of each of these several properties one normally would need a specific instrument with all its facilities and also people to use it. Therefore it can be assumed approximately that the n properties measured in a multi-purpose instrument are obtained for $1/n$ th of the cost it otherwise would be.

The merits of using a multi-purpose instrument discussed so far have already been pointed out briefly in a previous paper [1] by the author where research with a thermal conductivity cell was described.* The possibility of extending

* This work was supported by the National Science Foundation and the United States Army Research Office. Their help initiated and made possible the first steps towards the development of the multi-purpose instrument and is acknowledged with deep appreciation.

the capability of that instrument to that of a multi-purpose instrument was offered more or less self-evidently by using the cell. (This fact was also demonstrated in short in [1].)

As a result of these observations, an extensive analysis was initiated in 1964 to find the most feasible design. This was followed up with first sketches. A contract from the Air Force Office of Scientific Research then made it possible for the author to develop and to design the multi-purpose instrument at the Physikalisch Technische Bundesanstalt in Braunschweig during a leave of absence. Due to the fact that the previous investigations had gathered already important information the instrument not only was designed but also was built during a one year period of time.

MEASUREMENTS TECHNIQUE

Thermal Conductivity

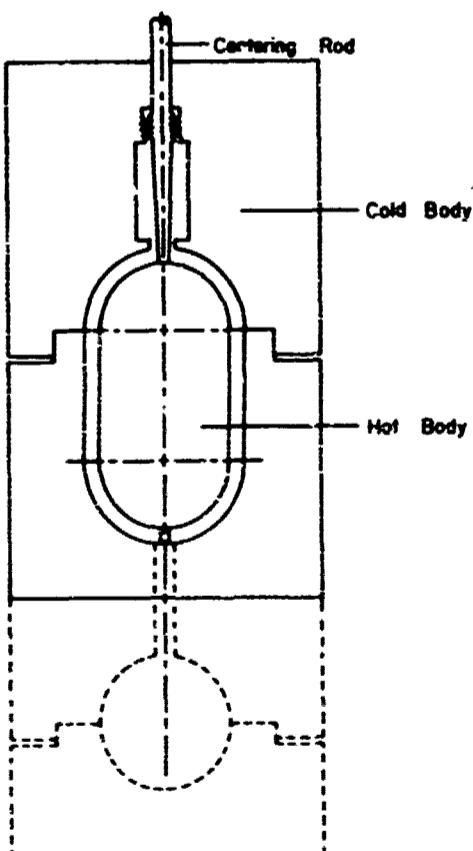


FIG 1 THERMAL CONDUCTIVITY CELL

The instrument for measuring thermal conductivity has been described in detail in [1] and therefore Fig. 1 only shows the cell schematically but in sufficient enough detail that the procedure necessary to extend its capabilities for the observation of other properties can be discussed.

The instrument consists of a cylindrical heater element (hot body) with hemispherical ends, placed and centered by means of a centering rod, within a similarly shaped but slightly larger cavity

of a cold body. The test fluid fills the gap between the two bodies. The arrangement operates without guard-heaters and allows therefore steady state to be reached in a short time, also of importance to avoid and/or minimize influences of temperature fluctuations.

In this case the thermal conductivity k can be readily obtained from Fourier's law

$$q_k = k \frac{A}{L} (T_{\text{hot}} - T_{\text{cold}}) \quad (1)$$

where

$$q_k = (V + \Delta V) (I + \Delta I) - q_r - q_c \pm q_L \pm (q_{\text{osc.}})_{\text{hot}} \pm (q_{\text{osc.}})_{\text{cold}} - (q_{\text{inh.}})_{\text{hot}} - (q_{\text{inh.}})_{\text{cold}} - (q_{\text{inh.}})_{\text{fluid}} \pm \dots \quad (1a)$$

is the heat flow by conduction, equal to the electrical power input corrected in order for radiation, convection, lead in losses, heat flow due to unsteady state condition and/or inhomogeneities. T_{hot} and T_{cold} are the surface temperatures of hot and cold bodies.

For absolute measurements it is necessary to determine the geometric constant of the arrangement, i.e., the ratio of overall heat transfer area and the average thickness of the fluid layer. The value is influenced by surface roughness and other inhomogeneities. The determination of the geometric constant can be done most accurately by measuring the electrical capacitance because all disturbances will be included. The capacitance measured will be

$$C = \epsilon_v \cdot \epsilon_g \cdot B \quad (2)$$

where $B = \frac{A}{L}$ = geometric constant

ϵ_v = capacitance of vacuum
 $= 8.8541735 \times 10^{-10}$ Farad/cm

ϵ_g = dielectric constant of the gas
 $= 1$ for vacuum

In a vacuum one observes the geometric constant

$$B = \frac{C}{\epsilon_v} \quad (2a)$$

directly and accurately when the centering rod enclosing the electric wires is built in such a way that lead-in capacities have no effect. This was achieved by a three-lead measurement technique [2].*

If the axis of the hot body coincides with that of the cold body the capacitance is then only a function of vertical displacement as shown in the upper part of Fig. 2. The almost parabolic capacitance curve has a minimum at a location of least disturbance, i.e., the most homogeneous field, which is therefore the best location of the hot body within the cavity of the cold body. For this setting, the value of the capacitance measured (and therefore the geometric constant) can be readily taken from the hundredfold magnified part of the curve in the neighborhood of the minimum as shown in the lower part of Fig. 2.

Dielectric Constant and Index of Refraction

Measurements of the capacitance when the instrument is filled with test fluid allows the determination of the dielectric constant of the test material with the aid of equation 2. The feasibility of this arrangement had been demonstrated in [1]. The data there observed are shown in Table 1.

The dielectric constant of many substances is proportional to the square of the index of refraction and therefore this third property can be determined simultaneously. The knowledge of the refractive index is of importance for the evaluation of radiant heat transfer which in turn is needed for computing the correct amount of heat transported by conduction only when thermal conductivity data are measured--see equation 1a.

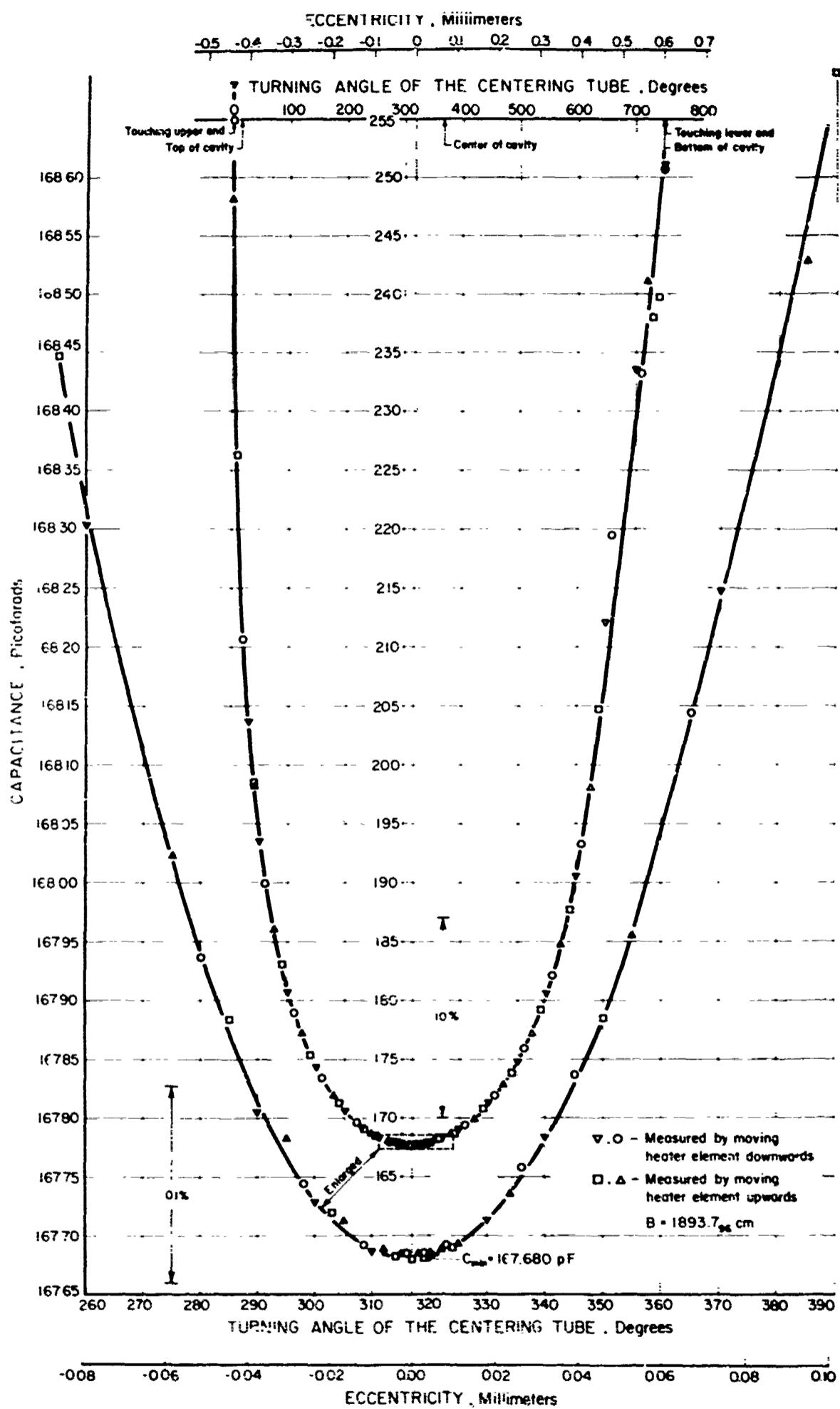


FIG. 2 MEASUREMENT OF THE GEOMETRIC CONSTANT, B

TABLE 1. DIELECTRIC CONSTANT OF SEVERAL TEST FLUIDS OF HIGHEST PURITY MEASURED UNDER NORMAL CONDITIONS

Material	Argon	CO ₂	Toulene
Temp., °C	25.04	24.00	----
Press., mm Hg	746.76	755.14	----
ε (measured)	1.0004932	1.000899	2.3787
N.B.S. value corrected for the same temp. & press.	1.0004996	1.0009038	2.379 (not corrected)
Departure	-6 pp m	-5 pp m	----

Electrical Conductivity (a.c.)

The capacitance bridge used for the measurements just discussed will yield a precision of six figures only if the loss is balanced equally precisely. The bridge then provides the dissipation factor D and/or the conductance of the sample for a particular frequency ω .

$$D = \omega RC \quad (3)$$

Therefore the electrical conductivity of the sample can be determined for the respective range of frequency.

Electrical Conductivity (d.c.)

The electrical wiring necessary to measure capacitance and/or a.c. conductance provides in addition to observe the d.c. conductivity of the test fluid by applying Ohm's law.

$$i = \lambda B \Delta P \quad (4)$$

where i is the current flowing through the test layer of geometry B under a potential difference ΔP of hot and cold body.

Thermal Expansion Coefficient of Instrument Material

Measuring in vacuum the capacitance of the arrangement as a function of temperature produces the geometric constant as a function of temperature due to the change of the geometrical arrangement as a result of the thermal expansion of hot and cold body. Equation 1 shows that the change in capacitance and/or geometric constant is directly proportional to the linear thermal expansion coefficient. But the value of this property will be correct only when the temperature change does not introduce at the same time a change in the position of the hot body in respect to the cold body surrounding it. Otherwise this would disturb the field resulting in an apparent increase of C and/or B. To hold the hot body in the same place in respect to the cold body under varying temperatures is possible only when the centering rod changes its length with temperature by an identical amount as the material of the cold body does. This can be achieved perfectly only when those two parts of the instrument are made out of the same material. The centering rod as already was pointed out must be built as a double electrical shield and it has to fulfill many additional and partially controversial requirements (this will be discussed later) and cannot be made out of the materials used for the cold body. As a result of this, there will be a displacement of the hot body within the cavity of the cold body. The error as a function of this eccentricity is shown in Fig. 3 (duplicating part of Fig. 4 of [1]) where the capacitance, made dimensionless with the minimum value, is plotted versus eccentricity. The curve of that figure represents the error due to eccentricity for the geometrical arrangement shown in Fig. 1 and when eccentricity exists only in the spherical part. It can be seen that axial displacement of 0.05 mm (i.e., 10% of thickness of layer of test fluid) results in an increase of capacitance and geometric constant

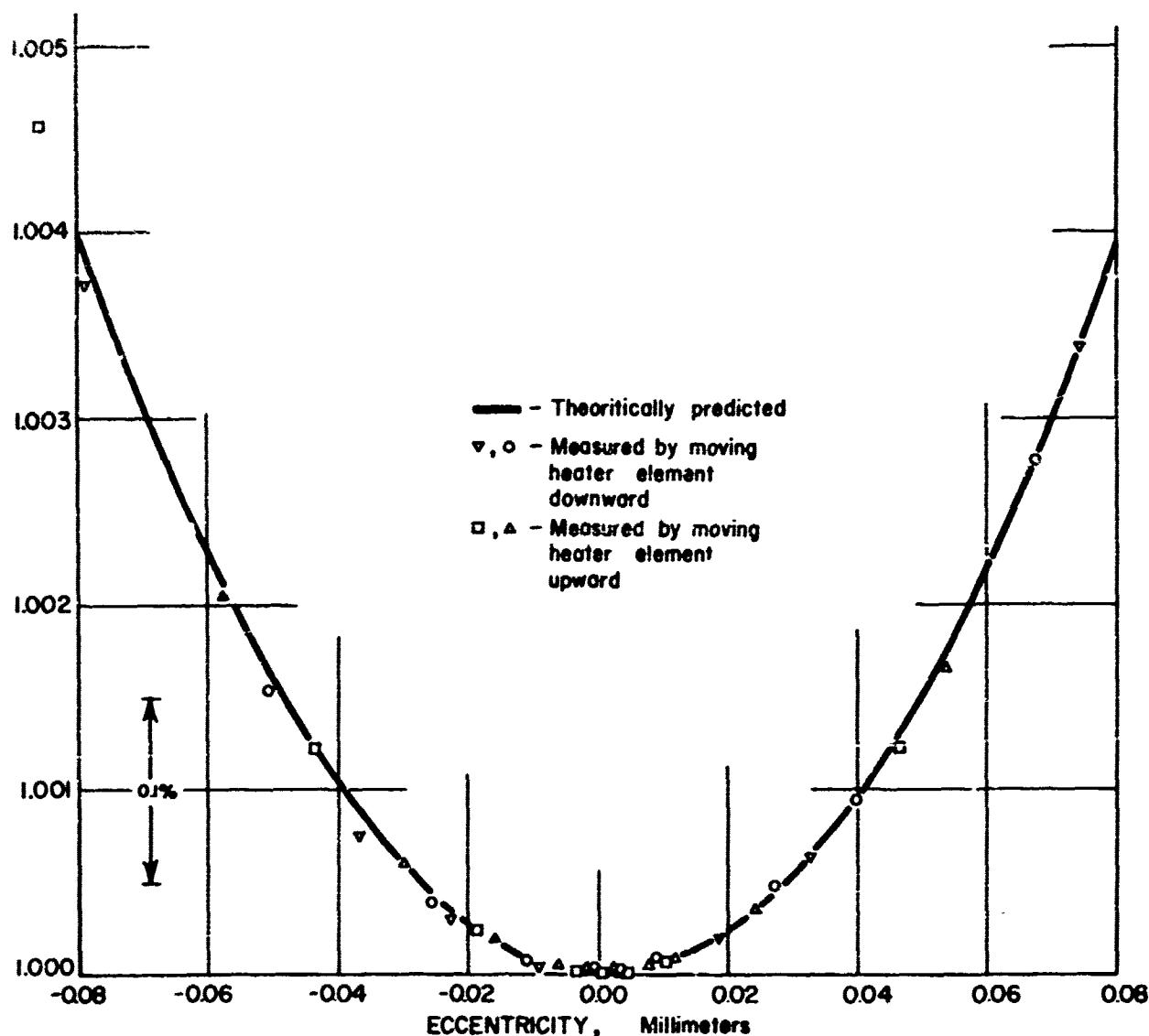


FIG. 3 ERROR DUE TO ECCENTRICITY

of only 0.15%. A displacement of less than 0.015 mm introduces errors of the order of one hundredth of a percent and becomes negligibly small. The discussion of the design of the centering rod will demonstrate that its composite structure can be designed such that it has a thermal expansion coefficient equal to that of the material of the cold body--but only for a certain temperature range. The thermal expansion coefficient for other ranges of temperature can be expected to be similar to the cold body material but not identical. Its true value can be determined with a high degree of accuracy by measuring the capacitance of the geometrical arrangement of the multi-purpose instrument first when the hot bdy is holding the centering rod and

secondly when the hot body rests on a piece of ceramic (the centering rod acts then only as a centering device but allows axial motions) so thick that minimum capacitance is achieved in accordance to Fig. 3. This thickness nominally is 0.5 mm and pure alumina would change its length in a 1000°C temperature range by a few thousandths of a millimeter. This expansion would displace the hot body in respect to the cold body cavity but according to Fig. 3 the influence of this displacement would have practically no effect on the capacitance values measured. In this case the true thermal expansion coefficient of the instrument material would be obtained.

Comparison of those correct capacitance measurements with those obtained when the centering rod fixes the position of the hot body yields the thermal expansion coefficient of the rod. This value is of interest only for determining the influence of changing inhomogeneities on the measurements of all properties where the geometric constant B is a major quantity.

Knowing the thermal expansion coefficient of the instrument material with the precision with which the capacitance measurements can be made makes it possible to determine the true volume occupied by the test fluid within the multi-purpose instrument at any temperature whenever the volume has been measured accurately at one temperature. This fact offers another possibility for using the multi-purpose instrument.

Thermodynamic p-v-T Properties of Gases and Vapors

Determinations of p-v-T relations in any kind of instrument is normally influenced most severely by the thermal expansion, introducing deviations from isochoric conditions. The multi-purpose instrument, as proven in the previous section, allows thermal expansion coefficient of the material of the instrument to be measured with a high precision, and therefore p-v-T data can be obtained accurately. The influence of pressure on the volume is much smaller than the temperature effect and can be made small by making the walls

of the instrument strong enough (thick enough and/or out of a material of high strength over the operating ranges of temperature). The change of volume with pressure can be determined accurately by capacitance measurements and when the instrument is charged with a gas of well known pressure dependence of its dielectric constant. If, in addition, its temperature dependence is known, the capacitance measurements will yield the change of volume with pressure and temperature. Accounting for the thermal expansion coefficient (measured as a function of temperature in the previous section) makes it possible to determine the volume change at different temperatures as a function of pressure only. With this information, Young's modulus of the wall material and its temperature dependence can be derived.

The pressure influence on the volume can be made negligibly small when the apparatus is held under the same pressure outside that exists inside. In this case only the compressibility of metals must be considered. Enclosing the apparatus in a high pressure vessel makes the instrumental setup somewhat more complex. The high pressure vessel must remain for reasons of size, cost a.o. near ambient, the instrument only undergoes temperature changes. The thermal insulation of the instrument will be pressurized and due to increasing free convection heat transfer becomes more and more ineffective with decreasing temperature and increasing pressure. As a result of this, the temperature range of the measurements with the instrument might be limited to such a temperature where the thermal load cannot be handled anymore by the thermostat.

The volume occupied by the test fluid within the multi-purpose instrument needed to be small for all the property measurements discussed under the sections on pages 3 through 7. For p-v-T data determination a larger volume is

more feasible and the best way to increase the space is to add another cavity to the instrument--most suitable in the shape of a sphere as indicated in Fig. 1 by dotted lines.

P-v-T measurements yield the compressibility factor. With known specific heat data then enthalpy, entropy, free energy and other thermodynamic functions can be derived from the measurements.

Vapor Pressure of Liquids

P-v-T data on gases and vapors can be conveniently observed only when condensation in a portion of the volume does not occur. Also, fluctuations in volume in the manometric section must be eliminated. A vapor pressure measuring device working at measuring temperatures and under isochoric conditions has been discussed in [1]. A similar but more sophisticated device will be used in the multi-purpose instrument--which then obviously can also be used to determine vapor pressure of liquids. As for vapor pressure data only, it is not necessary to know the composition of the liquid and vapor fractions.

Compressibility and Thermal Expansion Coefficient of Liquids

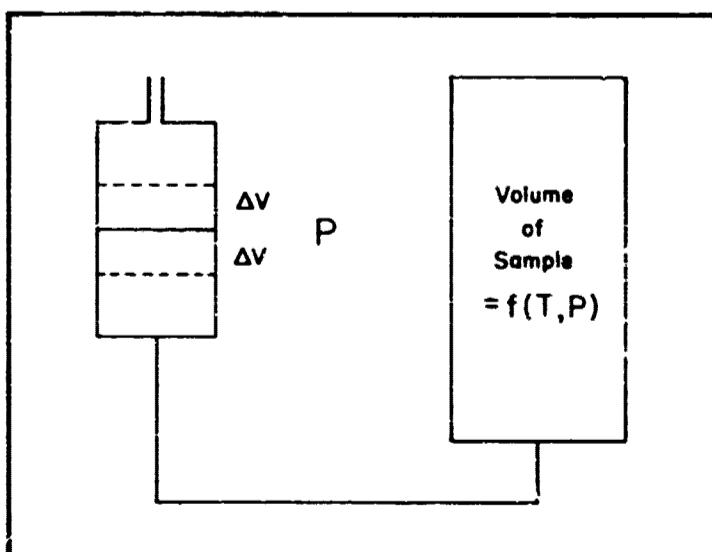


FIG 4 SCHEMATIC LAYOUT FOR EXPERIMENTAL SETUP TO MEASURE COEFFICIENTS OF THERMAL EXPANSION AND COMPRESSIBILITY

Connecting the multi-purpose instrument with external instrumentation by means of thin capillaries, as shown schematically in Fig. 4, makes it possible to observe the change of liquid level resulting from changing temperature and pressure of the test fluid within

the instrument. Accounting for the change of volume due to thermal expansion and/or under pressure of the material of the instrument yields then the thermal expansion coefficient and/or the coefficient of compressibility of the test fluid.

Errors in those determinations can be made small by avoiding change of volume with pressure and/or temperature of the external instrumentation and by eliminating effects of surface tension on the liquid level observed.

Specific Heats c_p and c_v of Liquids

E.O. Schmidt and the author described an adiabatic calorimeter [3] working in a quasi-steady state under continuous heating. The specific heat for this case is given by the equation

$$c = \frac{1}{m} \left(\frac{q}{T} - w_c \right) \quad (5)$$

where $\dot{T} = \frac{dT}{dt}$ is the temperature change with time of the test material observed under constant heat input q into a sample of heat capacity m_c being enclosed in a calorimeter body of heat capacity w_c .

The specific heat measured in an instrument like this will be of high accuracy whenever the constant and continuous heat input produces at any location within the sample the same temperature increase with time and whenever the temperature difference within the sample is so small that the specific heat can be assumed to be constant but large enough to detect the temperature change accurately.

These conditions can be provided, as was proved by the authors, by solving the partial differential equation describing the temperature field in the sample of spherical geometry under the assumptions that heat input to the sample takes place only at the surface of the heater element located at the center of the sphere, that there are no heat losses from

the outer surface and, finally, that at a time zero uniform temperature distribution T_0 exists within the sample.

The solution is given in Fig. 5 where the dimensionless temperature θ is plotted versus dimensionless time τ for different dimensionless locations ξ .

$$\theta = \frac{T - T_0}{q \cdot R} ; \quad \tau = \text{Fo}^* = \frac{a \cdot t}{R^2} ; \quad \xi = \frac{x}{R} ; \quad \zeta = \frac{r}{R}$$

with R the outer radius of the calorimeter,

r the outer radius of the heater of surface area A_r

k and a thermal conductivity and diffusivity of the sample.

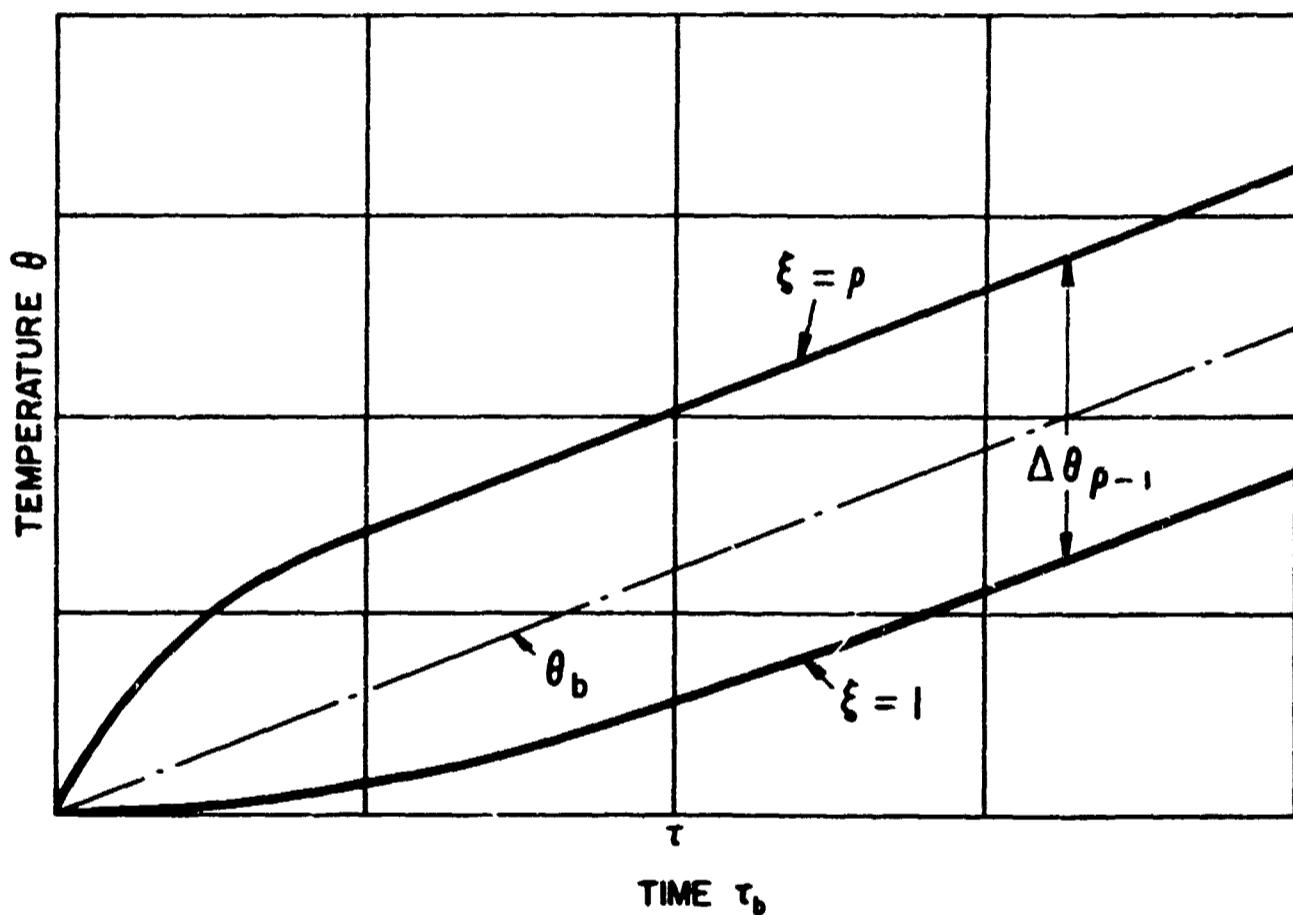


FIG. 5 TEMPERATURE CHANGE WITHIN THE CALORIMETER

At $\xi = \zeta$, i.e., at the surface of the heater element, the temperature of the sample increases first rapidly but then with decreasing slope until a constant rate is maintained. Due to finite thermal diffusivity, the heat input started at time zero causes, at the outer surface at location $\xi = \zeta$.

* Fo = Fourier number

first a slower change of temperature with time which then also continues at a constant rate. The constant rate of temperature change indicates quasi-steady state conditions. The bulk temperature of the sample increases from time zero on steadily--and the temperature difference within the sample remains constant for all times greater than τ_b . All measurements taken after time τ_b will yield the true specific heat at the respective temperature.

The analysis for other geometries of the sample, where the temperature field is dependent on more than one coordinate and influenced in addition by free convection heat transport within the sample is practically impossible to accomplish, but, on the other hand, solutions are not needed for those cases because the geometry of the sample is of less concern and free convection will increase the apparent diffusivity of the sample making measuring conditions more feasible than for the case of granular materials or very viscous fluids of low diffusivity as was considered by E.O. Schmidt and myself.

For these reasons the multi-purpose instrument also can be used to determine specific heats. The hot body will then be replaced by a calorimetric container of similar outside shape enclosing the sample of known mass. The cold body acts as an adiabatic envelope; its temperature must change in time by the same rate as the outside of the calorimeter does and the temperature difference between the two bodies must remain at zero. This requirement can be achieved by using the thermostat discussed in its own section on page 18.

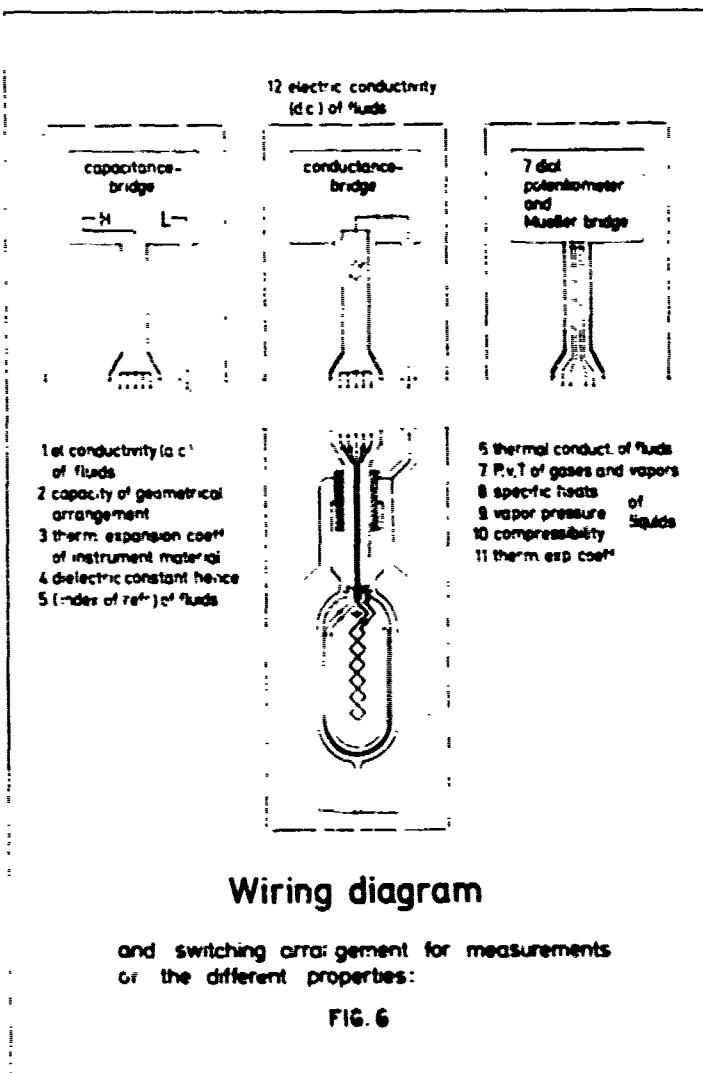
For measurements of specific heat c_p the calorimeter container will accomodate a bellow or other flexible device separating the liquid tested from a gas at constant pressure and allowing the test material to freely change its volume with temperature.

For measurements of c_v the same calorimeter arrangement can be used, but the flexible device can either be removed or inactivated and isochoric conditions are maintained.*

The steps discussed under Measurements Technique are necessary and more or less easy to achieve so that the capability of the thermal conductivity cell can be extended to that of a multi-purpose instrument. This instrument will be able to observe simultaneously six properties (k , ϵ , n , $\lambda_{a.c.}$, $\lambda_{d.c.}$, $p-v-T$) of the eleven listed when gases and vapors are tested and seven properties (k , ϵ , n , $\lambda_{a.c.}$, $\lambda_{d.c.}$, β , κ) when liquids are tested. Simultaneous in this

respect means that on the test fluid originally filled into the instrument all measurements are carried out and made possible by altering only outside connections as is schematically shown in Fig. 6, but the sample always remains the same. Therefore the different properties will be observed under perfectly identical conditions.

Those ideal situations cannot be provided for the other measurements. For specific heat determination the instrument itself must be altered and this



*The same arrangement can be used to measure the specific heat of solid materials as E.O. Schmidt and the author did.

necessitates moving the sample from the cell. Relocating the sample could be done by filling the calorimeter with the test substance being taken out of the instrument. Careful procedure should make it possible that the sample does not change during this process and when, in addition, the walls of the calorimeter and multi-purpose instrument being wetted by the test fluid have no effect, then a quasi-simultaneous determination of those properties are also possible and all data measured with the multi-purpose instrument will be obtained under practically identical conditions: pressure, temperature and impurity wise.

The techniques of measurement of the various properties with the multi-purpose instrument discussed so far represent first information towards a preliminary design but much more must be considered to reach the final design and to build the instrument.

BASIC DESIGN CONSIDERATIONS

Temperature and Pressure Measuring Ranges

One of the main requirements to be achieved by the multi-purpose instrument is to produce property data of high precision. The ranges of temperature and/or pressure must be chosen so that accurate measurements are not only possible but also made over a large range of these variables. For temperature, the working range of the instrument will be from -190°C to 650°C because in this range the platinum resistance thermometer is presently being recognized as standard for the international temperature scale. Selecting the temperature range limits to a certain extent the pressure range due to the strength of material of the instrument. Chosen was the range from vacuum to 500 atm which is felt sufficiently wide because the pressure dependence of many properties is small.

The ranges selected will be of influence on the design of the apparatus itself but more so in respect to the measurements with the instrument since all quantities needed to be observed for computing the various properties from the respective governing equations must be determinable accurately at any pressure and/or temperature. Pressure and temperature, in addition, must be precisely maintained at measuring conditions for at least that length of time needed to achieve steady state conditions and to take the readings.

Generating, changing, holding and measuring pressure can be done in most cases without difficulties but not for vapor and gas pressure under isochoric conditions. This will be discussed in more detail by dealing with the design of the instrument. Pressure, in addition, will be uniform within the instrument at any time and under any circumstances.

The situation is much more difficult in respect to temperature and considerable effort must be spent in theory, design and fabrication to overcome those difficulties or to minimize errors.

Thermostating the Instrument

Temperature regulation by means of electrical heating wires is insufficient because it is practically impossible to produce the same amount of heat per each length element of the heating wire and most of all uniform contact between wire and the walls of the instrument cannot be achieved. Furthermore, electrical heaters are useful only at temperatures above ambient; cooling by means of the Peltier effect is not effective enough in most cases.

Boiling point arrangements do promise excellent temperature control but changing from one value to the other needs pressure regulation over wide ranges and/or the use of different media.

Commercially available liquid thermostats operate very satisfactorily--but normally only in narrow ranges of temperature and, in addition, the use of different fluids is also required for different temperature ranges but those are not as wide as needed for the multi-purpose instrument.

It was therefore necessary to develop a new thermostat able to operate with one working media sensitively in the range required. A gas appears to be the best to use and helium was selected because its high thermal conductivity and low viscosity offer good heat transport capabilities.

The thermostat is shown schematically in Fig. 7. The helium is circulated by means of a pump in a closed loop. This loop consists of a bifilar^{*} coil and a heating section. A platinum resistance thermometer is used as a sensing element in an automatic control system. This system changes heat input and/or cooling in accordance to the deviation between the set value and that sensed by the resistance thermometer. Heating is regulated by changing the electrical power of the heater; cooling is regulated by means of two solenoid valves activated by the automatic control unit changing the amount of fraction of fluid flowing through the cooling coil and/or bypassing it.

In order to achieve high heat transport, the heat capacity of the helium is increased by pressure which is maintained by means of a storage tank. The pump has to overcome only the pressure drop of the high velocity flow within the closed loop.

* The thermostating fluid flowing through the instrument will decrease or increase in temperature according to the heat losses or gains. Therefore, at the exit its temperature will be higher or lower than at the inlet resulting in an uneven temperature distribution of the instrument. Arranging the flow bifilarly assumes uniform distribution because at every location the average temperature between the counterwise flowing fluid will be practically the same.

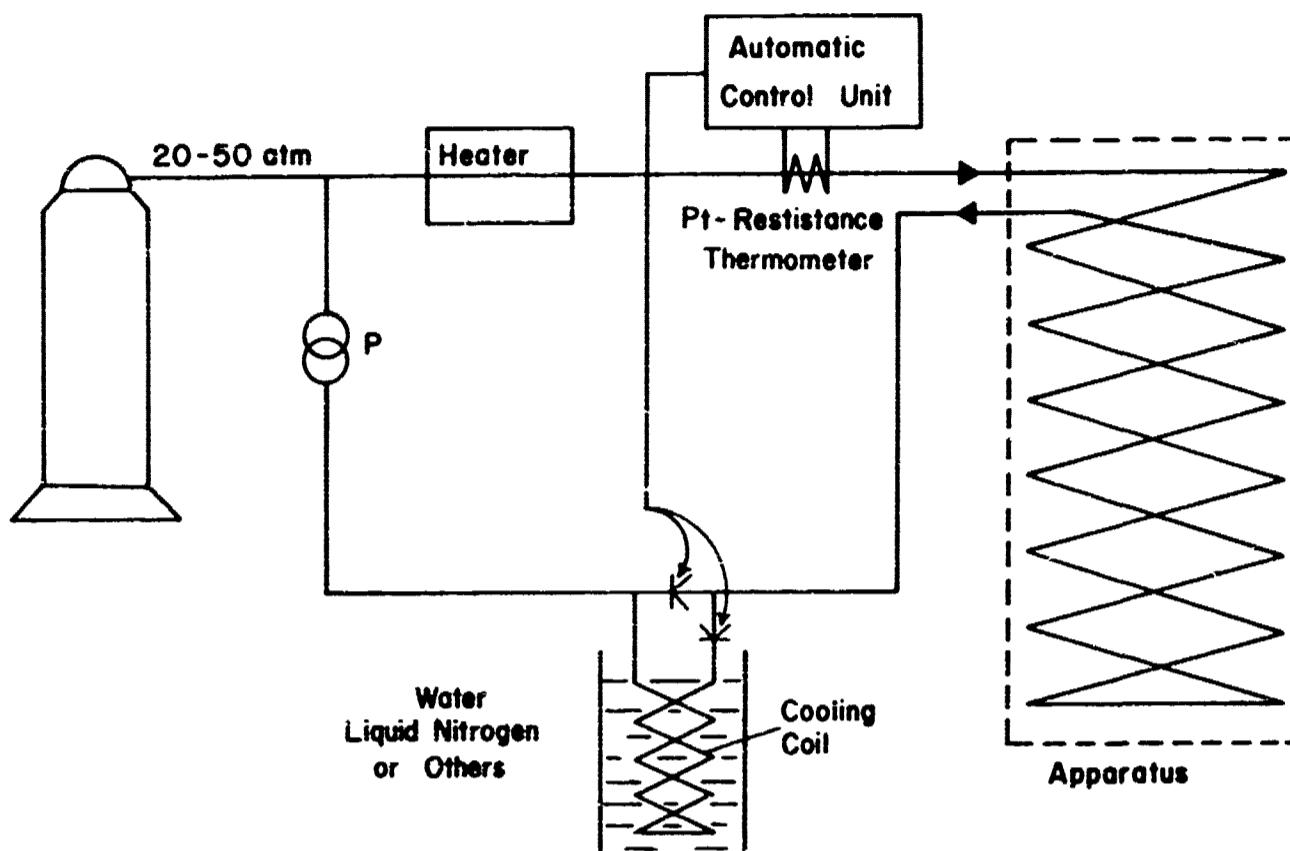


FIG. 7 THERMOSTAT

The thermostat arranged in this way was analyzed by the automatic control group of the Mechanical Engineering Department of Purdue University for the unfavorable case that the sensing element is not at the location shown in Fig. 7 but at the axis of an infinitely long cylinder of moderate diameter. Unfavorable for the reason that temperature changes and fluctuation at the surface penetrate only slowly into the interior and will therefore be noticed by the sensing element with a time lag--this can yield to an unstable control situation. For dimensions similar to that of the multi-purpose instrument and for reasonable loads and for properly chosen heat transfer conditions, it was proven by the analysis that even in the unfavorable case the temperature can be controlled with the sensitivity of the Pt-

resistance thermometer. Temperature fluctuation of the helium occur but with high frequency and low amplitude only.

This thermostat will make it possible to operate the multi-purpose instrument with the required sensitivity over the total range of temperature. The automatic control unit, in addition, can be programmed. The temperature of the instrument therefore can follow automatically such preset temperature-time-functions which allow for the heat capacities and transport conditions in the loop.

This is of importance in respect to the determinations of specific heat because adiabaticity requires that the cold body change its temperature in time in the same way as the calorimeter container does.

Providing Isothermal Conditions at Surfaces Wetted by Test Fluid

To make use of the possibilities offered by the thermostat, it is necessary to bring the helium in equal heat contact with every location of the apparatus. This is possible only when the material of the instrument is wetted by the heat transfer media directly. This can be achieved by cutting channels onto the surface as shown in Fig. 8--on the left hand side. Then the part of the surface occupied by the channel is in contact with the fluid only and not the bridges between them resulting in a different temperature at those locations--and an uneven temperature distribution of the surface. Assuming that the temperature of the thermostating fluid flowing through neighboring channels is the same (heat loss or gain is small) makes it possible to replace this distribution by a sine or cosine function allowing to determine by analysis the thickness of the wall necessary to dampen the uneven temperature distribution at the surface to negligibly small values at the inside of the instrument

being in contact with the material tested. The freehand field plot on the right hand side of Fig. 8 demonstrates that the dampening increases rapidly with thickness. The

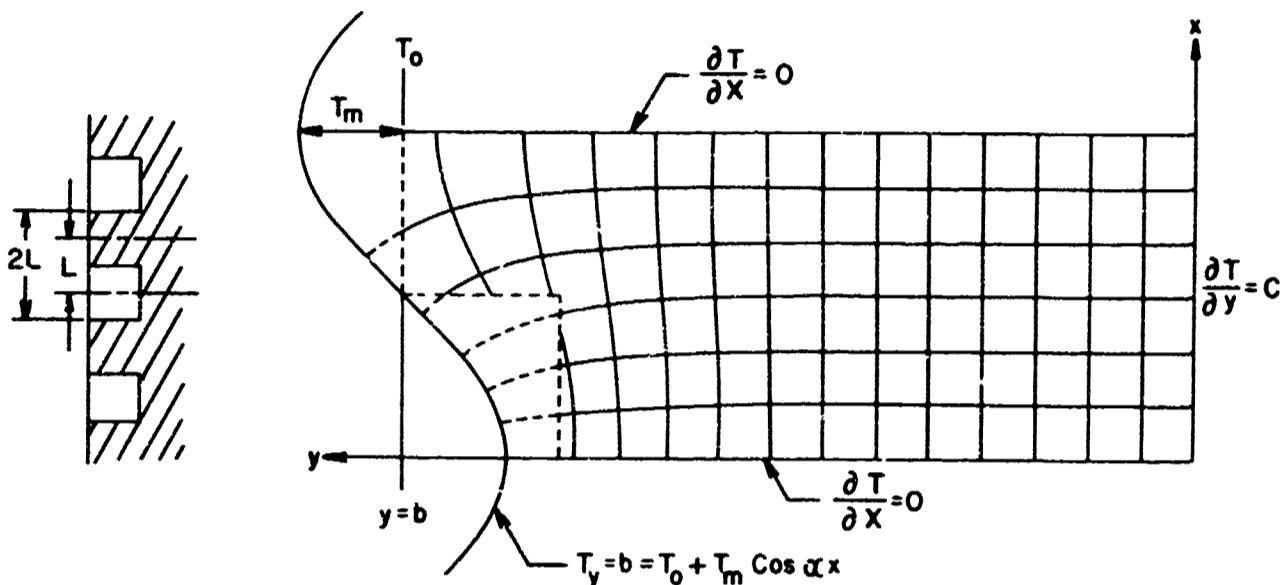


FIG. 8 INFLUENCE OF WALL THICKNESS ON TEMPERATURE DISTRIBUTION

one dimensional temperature distribution at the inner surface will be

$$T_{y=0} = T_o - \frac{q}{k_w} b + \frac{T_m}{\cosh \frac{\pi}{L} b} \cos \frac{\pi}{L} x \quad (6)$$

for a flat plate arrangement and the boundary conditions given in Fig. 8.

The second term on the right side of equation 6 indicates that the dampening is independent of the material of the wall but increases with the hyperbolic cosine of the wall thickness. For a thickness four times larger than the depth of the channels, the temperature at the inner surface will fluctuate by a 100,000 fold smaller amplitude T_m than at the outer surface. In addition, there will be dampening due to two dimensional heat flow. The walls of the multi-purpose instrument easily can be made thick enough to assure practically isothermal conditions at the surfaces wetted by the test fluid--this fulfills an important requirement for achieving

high accuracy especially for the determinations of thermodynamic properties. Isothermal surfaces, in addition, are a necessity for thermal conductivity measurements for the simple reason that otherwise the geometric constant must have a different and greater value than the one observed electrically where isopotential conditions will be present (to a large degree of certainty for the geometry chosen and for smooth surfaces). For achieving isothermal surfaces it is furthermore necessary that the heat flow coming from the hot body has everywhere an equal resistance to the heat sink--the cold body. This can be achieved, at least to a large extent, by providing equal distances, i.e., the outer contour of the instrument must be identical to that of the heater element--the hot body. Moreover, the heater element must be heated in such a way that there exists uniform heat flux from its surface.

Following the just discussed basic information towards a design will provide circumstances favorable for precise measurements but these ideal isothermal conditions must be disturbed by temperature measuring devices placed inside the wall. Those are needed first of all for determination of surface temperature when thermal conductivity is to be measured.

New Method for Elimination of Errors in Determination of Surface Temperature

Thermal conductivity data are of value to theoretical studies when their absolute accuracy approaches 0.1% or better. Assuming that all errors in the determination of heat flow, geometric constant is of the order of 0.05%, the temperature measurement must be made with the equal precision according to equation 1. This means that for a temperature difference across the layer of test fluid of one degree the temperatures of the surface of cold and hot body must be measured accurately within 2.5×10^{-4} degree.

Measurements of surface temperature is a major task in any kind of investigation and becomes obviously a very severe problem in our case. Measurements with thermocouples can be made sensitive enough but an extremely large effort must be spent and they are not reliable. Platinum resistance thermometers are very reliable and high precision can be reached relatively easy. Such elements offer, in addition, the observation of average temperatures of an infinite number of points along their stretch and not of one point only as a thermocouple does.

The surface itself cannot be made to be a resistance thermometer and it is necessary to place the sensing element somewhat beneath it into the wall. This fact introduces the problem of extrapolating the observed value to the correct surface temperature--and the more difficult task to evaluate the disturbance of the temperature field caused by the thermometers and the influence of those inhomogeneities on the temperature measurements and/or the value of properly determined.

This point is demonstrated in Fig. 9 showing at its left side the common arrangement, where the sensing element is located in a hole drilled parallel to the surface. The normal procedure to obtain the surface temperature is to evaluate the temperature drop within the wall due to conduction. This procedure is sufficiently accurate for many instances but not for precise measurements for many reasons. The true distance l cannot be determined properly for mechanical reasons and also due to the fact that it depends on the location of contact of the thermometer with the surface of the bore. The sensing element has a different thermal conductivity than the wall. Therefore, the temperature field is disturbed the heat flux and l change, as indicated in the field plot on the right hand side of Fig. 9.

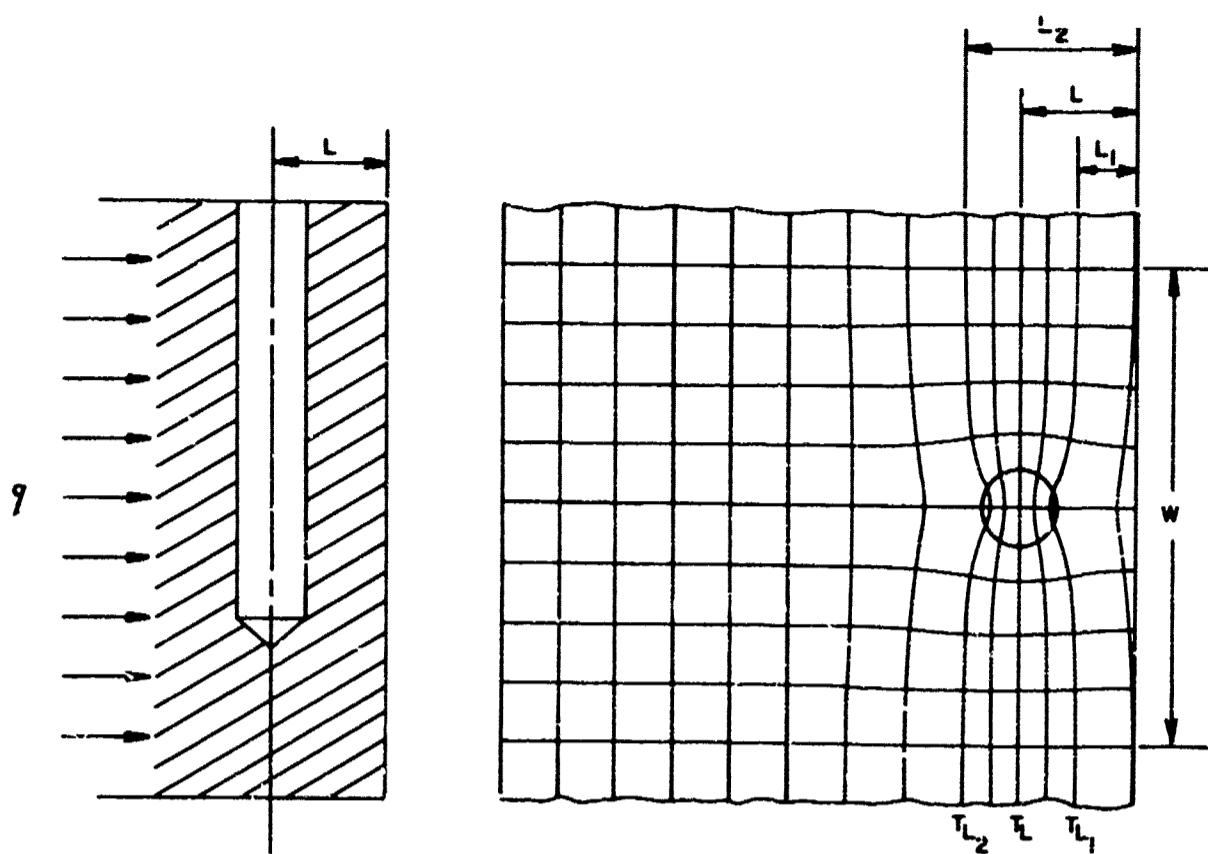


FIG. 9 DISTURBANCE OF TEMPERATURE FIELD

The thermometer located in the hole will measure any value of temperature between T_{11} and T_{12} depending on where contact with the surface of the bore² is made. If a uniform contact exists circumferentially * T_1 would be the temperature sensed and for this case the temperature drop within the wall evaluated with the wall thickness l would yield the surface temperature. For cases of temperature reading depending on contact location, different l 's must be applied. But the surface temperature evaluated would be the true one only for the surface outside the range W . To obtain the surface temperature within this range other values of heat flux and l must be used to compute the temperature drop.

* Equally good contact cannot practically be achieved and it is of advantage to surround the sensing element of the thermometer with an insulating material assuring a more uniform contact resistance--for steady state only for unsteady state measurements insulation would be of a disadvantage.

The part of the surface area of the hot body along the thermometer hole and of width W has a lower temperature than the remaining part of the surface. In the case of the cold body, the temperature of the respective area will be higher. Therefore, within the layer of test fluid an equally large area exists where ΔT is smaller and where less heat will be conducted. But this will be compensated for to a certain extent by the increase in B according to equation 1. How much the disturbances of the temperature field influence the desired accuracy anticipated can be judged only by computing the temperature field.

The disturbances obviously will be smaller the smaller the difference is in the values of thermal conductivity of the materials of the wall k_w and the hole k_h , respectively. A platinum resistance thermometer consists of wire and insulation material and its apparent thermal conductivity, i.e., k_h is practically fixed. Uniform conditions can, therefore, be provided only by choosing the material for the wall accordingly. But it must be pointed out that for this combination of low conducting materials the temperature drop across the sensing element is larger than with a wall material of high conductivity like copper. This is due to the fact that two dimensional heat flow (and possibly three dimensional heat flow for reasons of different contact resistance along the hole) will have more equalizing effect on the temperature distribution than in the case of low conducting wall material.

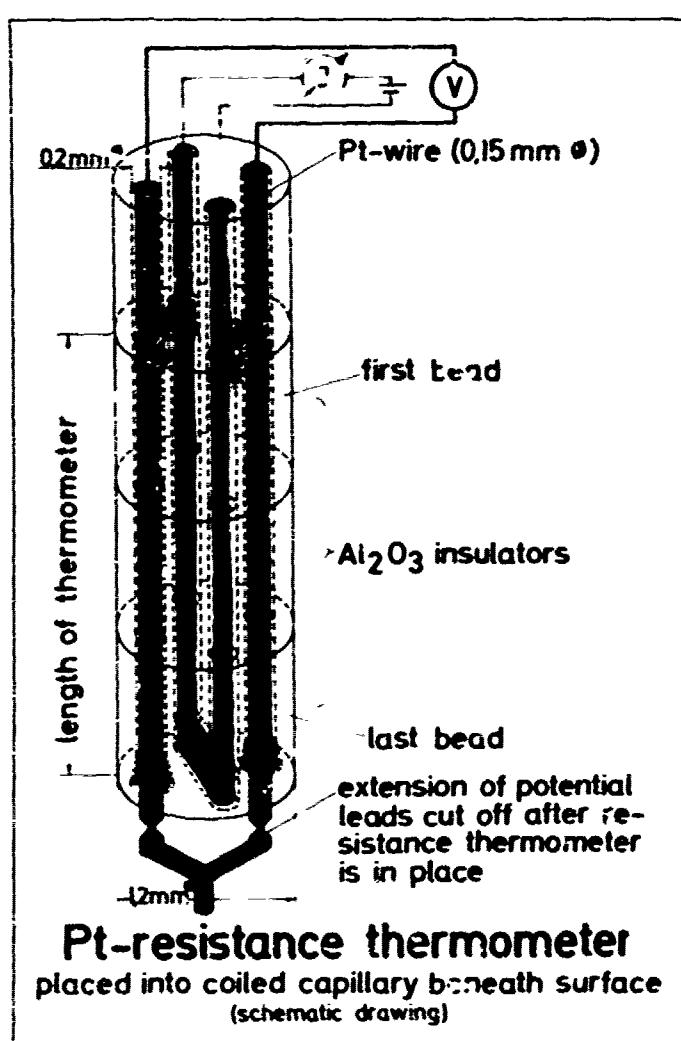
Despite this fact, a high nickel chromium alloy, Nimonic 80A* made by DEW, *** was chosen because of its

* The Curie-point of Nimonic materials is far outside the temperature range of our measurements.

** Deutsche Edelstahlwerke, Krefeld Germany

excellent mechanical properties at high and low temperatures and its equally good corrosion resistance make this material very suitable for the construction of the multi-purpose instrument. Its low thermal conductivity is a drawback only for the measurements of one property, the thermal conductivity, but this can be overcome by using specially designed resistance thermometers, placing them properly, and, finally, computing the temperature field.

Proper placement means that the location of the resistance thermometer must be definitely known in respect to the surface. This can be achieved by enclosing the thermometer in capillary tubes (made out of Nimonic 80A) which are hard soldered into grooves cut with proper shape and depth into the surface.



The resistance thermometer is of the form of a straight wire loop insulated by alumina beads as shown in Fig. 10. The clearance of the beads inside the capillary tube is of the order of .1mm and less. The large number of beads used and the small clearance will assure that contacts are made at many different locations lengthwise and in respect to the circumference of the inside surface, thus helping to observe average temperature. This is supported also by the fact that the parallel

wires of the resistance thermometer are twisted and therefore see similarly different locations of the enveloping material. Cutting the grooves with a lead onto the cylindrical surfaces of the instrument improves, in addition, the reading of the average temperature of the total surface. The straight wire arrangement of the resistance thermometer and enclosing it by materials of thermal expansion close to that of platinum assures that the resistance thermometer, once put in place and properly annealed, will be subjected to least stress and its temperature dependent resistivity will remain constant to a large extent.

The technique of measuring surface temperature just discussed yields the composite structure of the multi-purpose instrument shown in Fig. 11. To the Nimonic surfaces

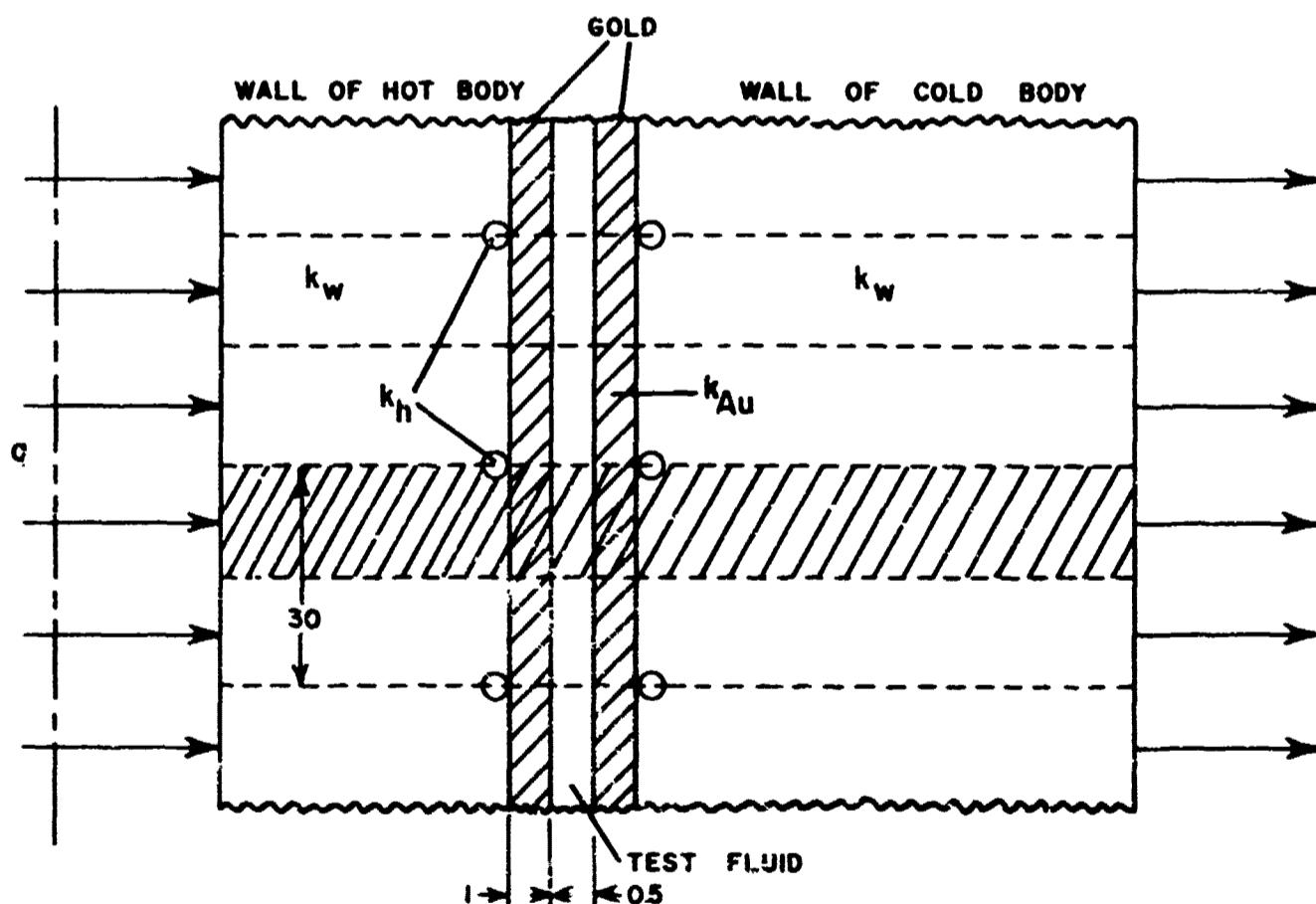


FIG. 11 CROSS-SECTION OF COMPOSITE STRUCTURE

are bonded pure gold layers of 1 mm thickness for reasons of keeping radiant heat transfer small, to avoid chemical reaction with the test fluid, etc.

The temperature field for steady heat flow was computed by a relaxation method under the assumption that cold and hot bodies are infinitely long cylinders. The gap accomodating the test fluid of nominal 0.5 mm width represents the distance between nodal points in radial direction. The arrangement is radially symmetric and therefore only a section like the shaded one needs to be considered; its height is given by the lead of the capillaries enclosing the resistance thermometer and the symmetry. Distances between nodal points in axial direction have been chosen to be 1mm. For simplicities sake the 1 mm^2 circular section of the resistance thermometer was replaced by a rectangle $0.5 \times 2 \text{ mm}$. For the wall-thickness of the cold body of the multi-purpose instrument computed in the previous section and for a diameter of the hot body of 34 mm enclosing an electrical heater of 8 mm diameter one obtains 1200 nodal points; i.e., 1200 equations with 1200 unknowns must be solved to obtain the temperature field in the composite structure. The large number of equations, the cylindrical geometry and the different properties involved make it obvious that solutions can be obtained by an iteration procedure only and only with the aid of large computers. It might be for this reason that solutions of the problem have not yet been available--also for the fact that programming by itself represents a very time consuming task. Allision Division of General Motors Corporation in Indianapolis fortunately had worked out a program for similar studies and they generously allowed the use of their facilities. This is greatly appreciated and Mr. Pyne and Mr. Colborn of Allision are thanked for their help and work.

The computation of the temperature field was carried out for various arrangements and especially for three different fluids within the gap selected in respect to the range of thermal conductivity values to be measured with the multi-purpose instrument.

The results of the calculations are given in Tables 2, 3, and 4 where the temperatures of the nodal points in the neighborhood of the surfaces of hot and cold body are recorded. Table 2 shows the temperature field for the case that the test fluid is of low conductivity (10 times smaller than that of water) and for a steady heat flow through the composite structure producing one degree temperature drop in the sample.

TABLE 2. STEADY STATE TEMPERATURE DISTRIBUTION IN WALLS OF INSTRUMENT ADJACENT TO SURFACES WETTED BY A FLUID ($k_{\text{fluid}} = 0.1 k_{\text{water}}$; $\Delta T = 1^{\circ}\text{C}$)

25	26	27	28	29	30	31	32	33	34
2617.1	2616.7	2615.7	2615.7	2615.7	2514.5	2514.5	2514.5	2512.7	2512.3
2617.0	2616.5	2615.7	2615.7	2615.7	2514.5	2514.5	2514.5	2512.8	2512.4
2616.9	2616.3	2615.8	2615.7	2615.7	2514.5	2514.5	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.7	2615.7	2514.5	2514.5	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.7	2615.7	2514.5	2514.5	2514.4	2514.0	2513.5
2615.8	2616.3	2615.8	2615.7	2615.7	2514.5	2514.5	2514.4	2514.0	2513.5
2616.8	2616.3	2615.8	2615.8	2615.7	2514.5	2514.5	2514.4	2514.0	2513.5
2616.8	2616.3	2615.8	2615.8	2615.7	2514.5	2514.5	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.8	2615.7	2514.5	2514.4	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.8	2615.7	2514.5	2514.4	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.8	2615.7	2514.5	2514.4	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.8	2615.7	2514.5	2514.4	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.8	2615.7	2514.5	2514.4	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.8	2615.7	2514.5	2514.4	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.8	2615.7	2514.5	2514.4	2514.4	2514.0	2513.5
2616.9	2616.3	2615.8	2615.8	2615.7	2514.5	2514.4	2514.4	2514.0	2513.5

The nodal points are counted in radial direction starting at the heater element of the hot body and in vertical direction from the adiabatic line going through the thermometer. The temperature of nodal points on this line are represented by the values listed directly under the numbering of the radial subdivision. The surfaces of the hot and cold body are located at number twenty-nine and thirty, respectively-- indicated in the table by vertical lines. The rows of values under these numbers represent the temperature distribution of the respective surfaces. The gold coat occupies the layer between 27 and 29 and between 30 and 32. The temperature measured by the thermometers will be an average of the values given for the nodal points at the location indicated and by taking into account the symmetry of the arrangement.

The temperature values are given to a thousandths of a degree (i.e., 2615.7 must be read 26.157°C). An inspection of the table indicated the disturbance of the temperature field in the neighborhood of the thermometers. The result that the gold layer dampens that disturbance completely is important; the surface remains isothermal. For this case the geometric constant is identical to that one determined by capacitance measurements. The true temperature drop within the wall can readily be obtained from the table. This information will be helpful to achieve a more accurate extrapolation from the temperature read by the thermometer to the surface temperature whenever thermal conductivity of different fluids and/or under different conditions in the gap will be determined. For this reason the computation was repeated for the same substance but under a heat flow increased by a factor of two; therefore, there is a two degree temperature difference between hot and cold body surfaces. (This also represents conditions within the walls one would obtain when a fluid of twice the thermal conductivity is investigated.)

TABLE 3. STEADY STATE TEMPERATURE DISTRIBUTION IN
WALLS OF INSTRUMENT ADJACENT TO SURFACES
WETTED BY A FLUID ($k_{\text{fluid}} = 0.1 k_{\text{water}}$; $T = 2^{\circ}\text{C}$)

25	26	27	28	29	30	31	32	33	34
2732.4	2731.6	2729.8	2729.7	2729.7	2530.1	2530.2	2530.2	2528.8	2528.3
2732.2	2731.2	2729.8	2729.8	2729.7	2530.2	2530.2	2530.2	2529.1	2528.5
2732.0	2730.9	2729.8	2729.8	2729.7	2530.2	2530.2	2530.1	2529.3	2528.6
2731.9	2730.9	2729.8	2729.8	2729.8	2530.2	2530.2	2530.1	2529.4	2528.6
2731.9	2730.9	2729.8	2729.8	2729.8	2530.2	2530.2	2530.1	2529.4	2528.7
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.2	2530.1	2529.4	2528.7
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.1	2530.1	2529.4	2528.7
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.1	2530.1	2529.4	2528.7
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.1	2530.1	2529.4	2528.7
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.1	2530.1	2529.4	2528.6
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.1	2530.1	2529.4	2528.6
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.1	2530.1	2529.4	2528.6
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.1	2530.1	2529.4	2528.6
2731.9	2730.9	2729.9	2729.8	2729.8	2530.2	2530.1	2530.1	2529.4	2528.6

The results are given in Table 3. There it can be noticed that the disturbance of the temperature field is increased and the surfaces are no longer isothermal. But the deviation from uniformity is small and only present in the immediate neighborhood of the thermometer--the area influenced is only a small fraction of the total heat transfer area. The evaluation of the true surface temperature and of the true temperature difference is somewhat more involved and the

geometric constant must be corrected to a slightly higher value. The disturbances are small, can be taken into account and will have little influence on the final result--the value of the property measured.

The two cases discussed so far represent conditions similar to those present in the multi-purpose instrument when thermal conductivity of most gases, vapors and liquids are measured. Therefore, tests with those fluids can be made with high precision.

TABLE 4. STEADY STATE TEMPERATURE DISTRIBUTION IN WALLS OF INSTRUMENT ADJACENT TO SURFACES WETTED BY A FLUID ($k_{\text{fluid}} = k_{\text{water}}$, $\Delta T = 1^{\circ}\text{C}$)

25	26	27	28	29	30	31	32	33	34
2762.2	2758.2	2749.1	2749.0	2748.9	2653.6	2653.4	2653.3	2647.1	2644.7
2761.1	2756.2	2749.2	2749.0	2748.9	2653.5	2653.4	2652.2	2648.4	2645.4
2760.1	2754.7	2749.4	2749.1	2749.9	2653.5	2653.3	2653.1	2649.4	2641.0
2759.8	2754.5	2749.4	2749.2	2749.0	2653.4	2653.2	2653.0	2649.5	2646.2
2754.7	2754.4	2749.4	2749.2	2749.0	2653.4	2653.2	2653.0	2649.6	2646.3
2759.6	2754.4	2749.5	2749.3	2749.1	2653.3	2653.2	2653.0	2649.6	2646.3
2759.5	2754.4	2749.5	2749.4	2749.1	2653.3	2653.1	2653.0	2649.5	2646.3
2759.6	2754.4	2749.5	2749.3	2749.1	2653.3	2653.1	2652.9	2649.5	2646.3
2754.7	2754.5	2749.5	2749.3	2749.1	2653.3	2653.1	2652.9	2649.5	2646.3
2759.7	2754.5	2749.6	2749.4	2749.2	2653.3	2653.1	2652.9	2649.5	2646.3
2759.7	2754.5	2749.6	2749.4	2749.2	2653.3	2653.1	2652.9	2649.5	2646.3
2759.7	2754.5	2749.6	2749.4	2749.2	2653.3	2653.1	2652.9	2649.5	2646.2
2759.7	2754.5	2749.6	2749.4	2749.2	2653.3	2653.1	2652.9	2649.5	2646.2
2759.7	2754.5	2749.6	2749.4	2749.2	2653.2	2652.1	2652.9	2649.5	2646.2
2759.7	2754.5	2749.6	2749.4	2749.2	2653.2	2652.1	2652.9	2649.5	2646.2

The situation becomes more difficult when materials of high conductivity are measured. This is proven in Table 4 showing the temperature distribution in the multi-purpose instrument when water is the test fluid and there is one degree temperature difference in the test layer. The surfaces deviate now from being isothermal for an extended heat transfer area, but practically half of it remains at a uniform temperature. The corrections necessary are more severe and more difficult to perform but they can be made with a high degree of certainty due to the information given by the analysis.

The computation has been carried out with preliminary dimensions provided by first sketches of the multi-purpose instrument. The correct dimensions are now available by the final design and the computation will be repeated before measurements start and they will be carried out to a ten thousandths of a degree of the temperature values.

The determination of surface temperature together with the evaluation of radiant heat exchange and lead-in losses did represent the most severe obstacles in achieving good precision in thermal conductivity research. The analysis performed, the special design and fabrication will increase the accuracy of property data measured and of all other investigations where the surface temperature is a major quantity and for all this it can be hoped that the benefits resulting from it will justify the effort spent.

TIME NEEDED TO ESTABLISH STEADY STATE
TEMPERATURE CONDITIONS

The multi-purpose instrument will operate over wide temperature ranges and the measurements of the different properties will be made at different levels of temperature. Changing from one level of temperature to another can be done conveniently with the aid of the thermostat but the question

remains if the new steady state conditions necessary for the measurements can be reached in a reasonably short time--especially in the instrument constructed out of a material which has been selected because of its mechanical and chemical qualities and also, to a certain extent, because of its low thermal conductivity. The low diffusivity of the nickel-chromium alloy will influence the time needed for heating or cooling the instrument to a new temperature level but not to the extent its low diffusivity indicates at a first glance. The heat transfer coefficient of the helium flowing through the channels of the instrument has a stronger effect. This is proven in Fig. 12. The graph given there represents the solution of the differential equation describing

the temperature change in infinitely long cylinders heated or cooled by convective heat transfer [4] under the assumption that the heat transfer media remains always at a constant temperature. The plot shows the time needed to decrease the temperature difference between helium and inside of the cylinder to one percent of the original value and when the cylinder originally

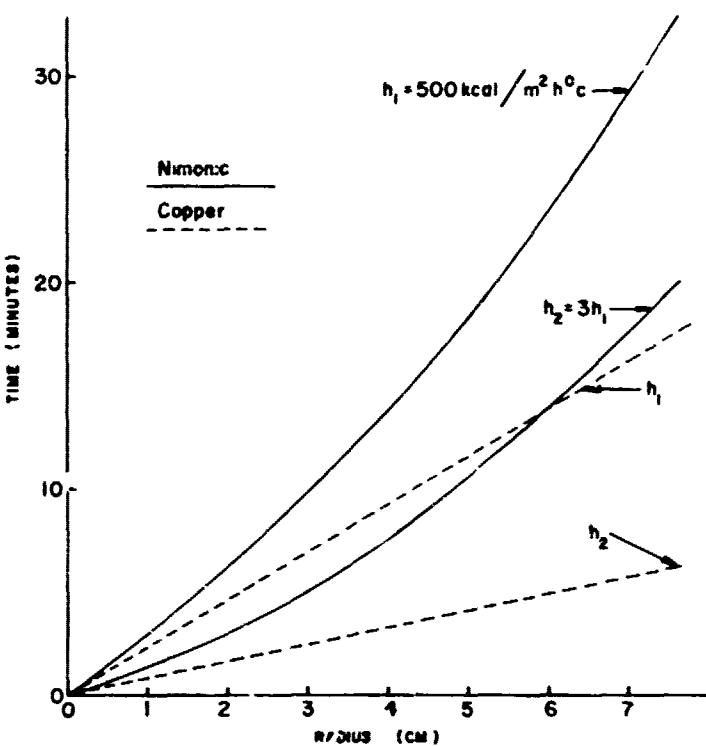


FIG.12 TRANSIENT HEATING OF CYLINDERS

was at a uniform temperature.

The time needed is plotted versus size of the cylinder made out of copper and Nimonic for two different heat transfer conditions. For a heat transfer coefficient of about $500 \text{ kcal/m}^2 \text{ h}^\circ\text{C}$ a copper cylinder of 50 mm radius would reach the new temperature level in 11 minutes--the Nimonic

cylinder in nineteen minutes. Not even twice the time is needed to heat the body of twenty times lower diffusivity.

For three times higher heat transfer coefficient and for the same geometry the times needed would be four and eleven minutes respectively. For an infinitely high heat transfer, a Nimonic cylinder would need twenty fold more time than a copper cylinder--but this is practically of no concern since the absolute times involved are small anyhow.

The same holds true for the case of lower convective heat transfer because the waiting time to achieve other conditions for new measurements is smaller than the time needed to prepare for the new observations. Not taken into account is the time needed by the thermostat to change the temperature of the helium to a new level. This will not influence the conditions to a large extent because in a normal case helium and the instrument will be heated or cooled simultaneously.

Everything described so far discussed the necessary steps to be taken to extend the capability of a thermal conductivity cell to that of a multi-purpose instrument and demonstrated the approaches needed to achieve reliable measurement of the different properties. This discussion also proved that a design of such an instrument was feasible but this does not necessarily mean that it can be built--especially in respect to the centering rod--the most critical and important part of the apparatus. Therefore, the task to be performed before work on the design could be started was to investigate the possibilities of fabricating the centering rod.

THE CENTERING ROD

The centering rod has to fulfill many and partially controversial requirements as already was stated briefly. It encloses all lead-in wires to the hot body and must be built as a double electrical shield for electrical reasons. It

must be thin walled and of small cross-sectional area in order to minimize heat losses from the hot body. (For the same reason there should be a certain amount of heat generated within the centering rod.) It must be strong enough to withstand outside pressure up to 500 atm and 650°C and it must be able to resist buckling under heavy axial loads. Last but not least, it must have a thermal expansion coefficient identical or at least close to that of the material of the cold body surrounding it (as discussed on page 8). Converting the thermal conductivity cell to a multi-purpose instrument could not be done when the electrical requirement of double electrical shielding was impossible to achieve. Therefore, the point had to be considered first. Electrical shielding requires a combination of conducting and insulating materials. The pressure and temperature ranges chosen for the operation of the instrument necessitates the use of high-strength metals and ceramic. The latter must have excellent electrical and mechanical properties and, in addition, equally good chemical resistivity. Alumina of high purity fulfills those requirements. Combining this ceramic with a metal to achieve pressure leak-proof conditions for all temperature ranges needs a hard soldering process. This soldering can be done only when the thermal expansion coefficients of the two components match over the range of temperature. Iron-nickel-cobalt alloys fulfill this requirement closely, and the best combination for our range of temperatures is Vacon 70 of Vacuum-schmelze, Hanau and Al8 type aluminumoxyd (88%) of Stemag, Lauf. Making the metallic Vacon 70 parts thin walled and of a shape which allows some spring action assures perfect combinations even when the thermal expansion coefficients are not perfectly identical.

The aluminum oxide insulators hard soldered to Vacon 70 material occupy a certain length of the centering rod and for this length the thermal expansion coefficient is much smaller than that of the material of the cold body. To

fulfill the requirements of least heat loss from the hot body it was necessary to make the connecting tube thin walled and this in turn dictated the selection of the material for reasons of strength. Nimonic 90 was chosen but this material also has a thermal expansion coefficient that is smaller than Nimonic 80A. In order to compensate for the difference it was necessary to use for the extension of the centering rod another material, ATS 15, having a thermal expansion coefficient much higher than that of Nimonic 80A and to select the length of the Nimonic 90 and ATS 15 parts so that for the total length of the centering rod a thermal expansion coefficient obtained is equal to that of Nimonic 80A. This will be equal only for a certain temperature condition. For other temperatures there cannot be a perfect match for the simple reason that the temperature dependence of thermal expansion coefficients of the materials involved are not identical. But they are similar and therefore the centering rod will change its length with temperature not much differently than the cold body does, and only a small displacement of the hot body in respect to its surroundings will occur. This will change the geometric constant, but this will be measured and its true value will be known at any temperature as discussed on page 8. The increase of inhomogeneities will be of little effect on the property determinations. The small difference in thermal expansion is equally important to assure that the hot body never can be displaced within its surroundings to such an extent that contact with the cold body occurs which would make measurements impossible and damage the instrument.

Combining the different metallic parts (most of which are thin walled) can be done only by electron-beam welding. The feasibility of the construction just discussed was tested on a pilot device and then designed. This did lead to the arrangement shown in Fig. 13. The centering rod is

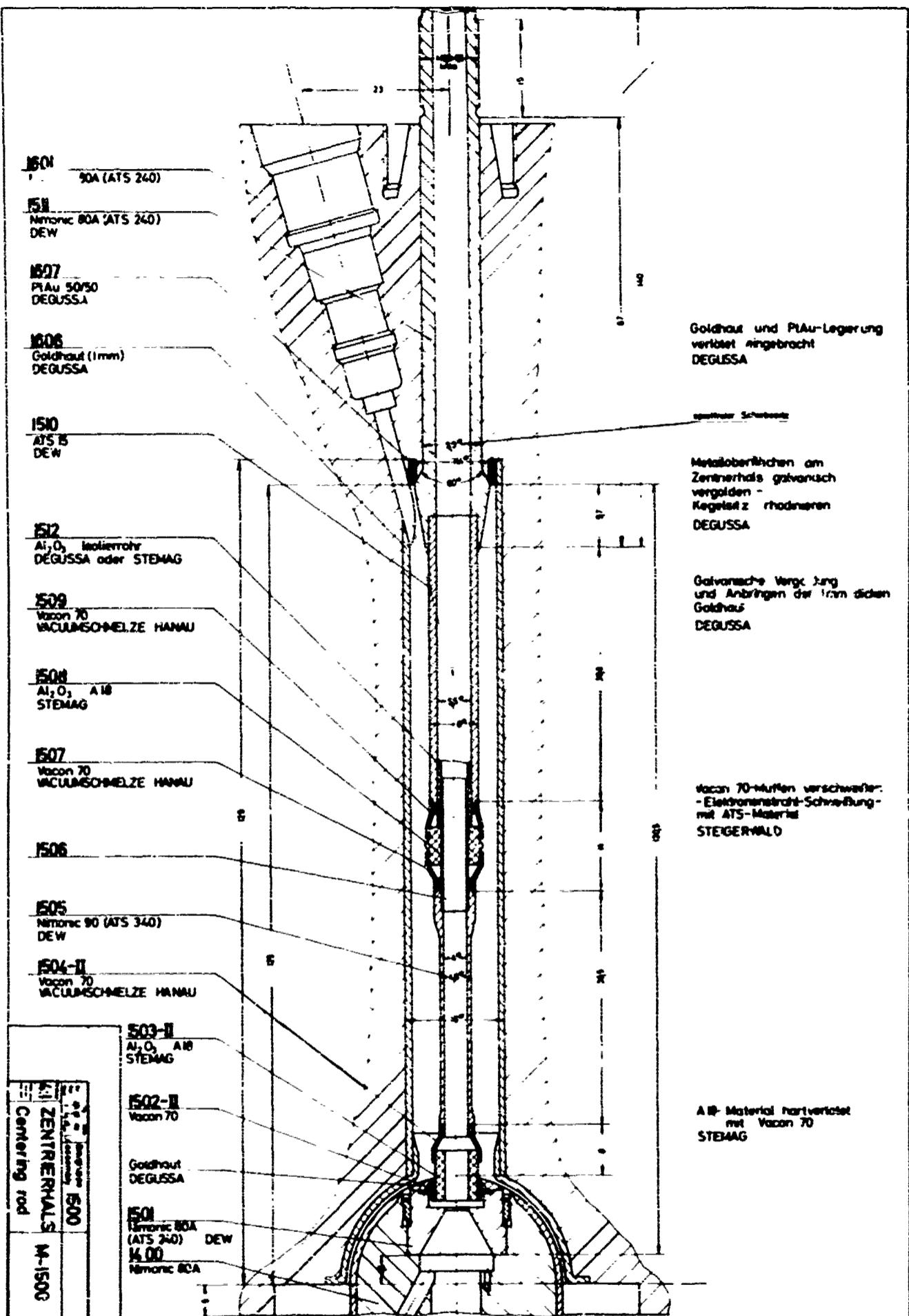


FIGURE 13. CENTERING ROD

perfectly aligned and attached to the hot body by means of its base held in place by a screw arrangement. The centering of the hot body within the cold body's cavity is achieved by a honed hole in the axis of the cold body accomodating the cylindrical extension of the centering rod with least clearance. Pressure tight seal is provided by a 60° tapered seat and a gold gasket of a thickness chosen in respect to the proper placement in axial direction and to achieve the setting where minimum value of capacitance was observed. Sealing forces onto the gasket are applied by means of a sleeve and screw allowing the centering rod to be pulled in an upward direction (these are not shown in Fig. 13).

The tube 1505 and its extension 1506 shield the lead-in wires and are shielded themselves by tubes 1510 and 1511 in order to accomplish the electrical measurements as discussed previously.

Fig. 13 is a reproduction of the assembly drawing of the centering rod. On the left hand side are given the numbers of the parts and the respective materials they are made from and also the vendors and/or producers of the materials. On the right hand side are listed the necessary steps to be taken to construct the centering rod.

THE FINAL DESIGN OF THE INSTRUMENT

The design of all the other parts of the multi-purpose instrument was somewhat less involved than the development of the centering rod and lead to the apparatus shown in Fig. 14. The cross sectional view represents the reproduction of the engineering drawing somewhat modified for easier reading.

The instrument consists of four major parts: the hot body and the three parts assembling the cold body. The cold body has two cavities--the upper one of proper shape to

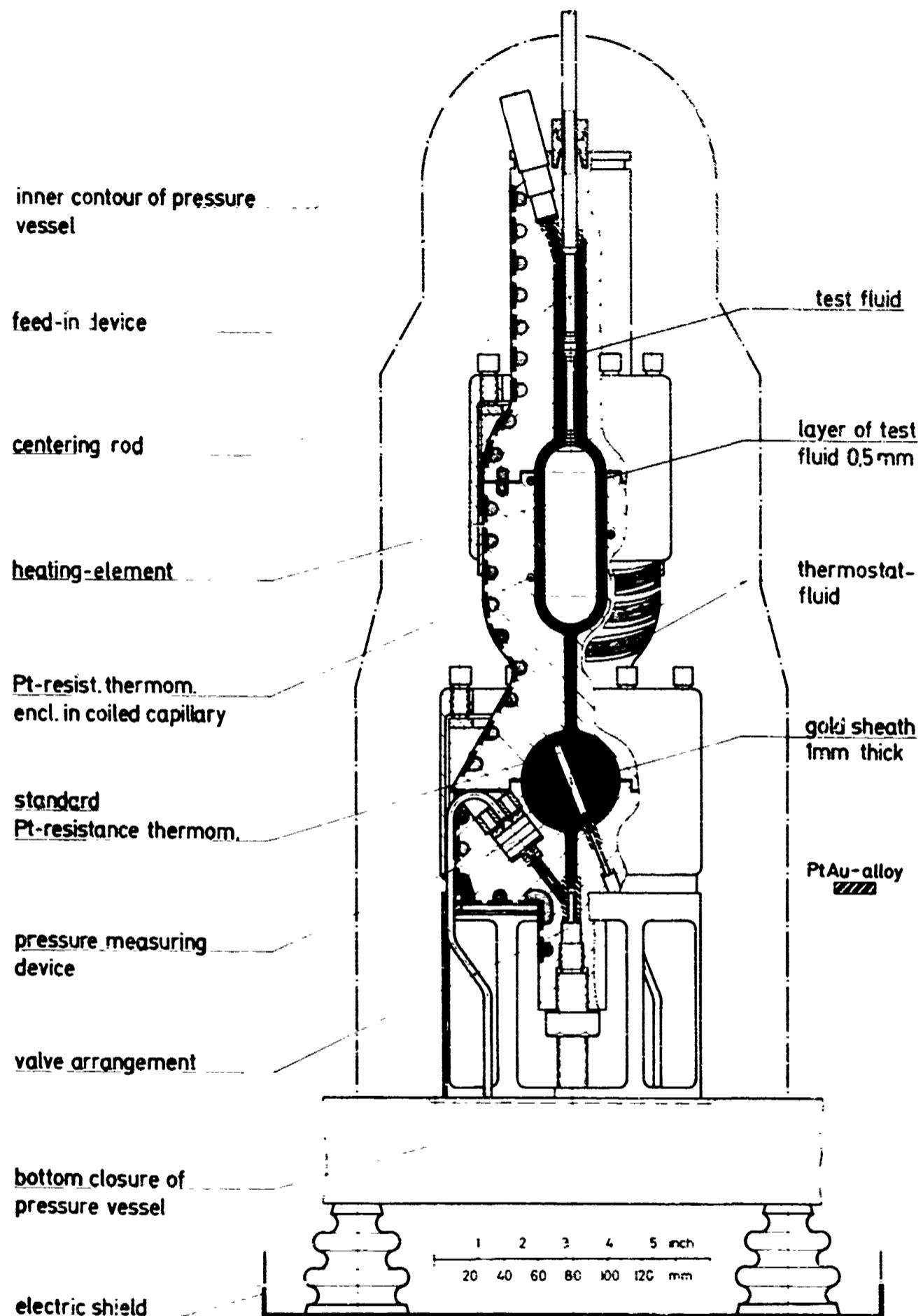


FIGURE 14. MULTI-PURPOSE INSTRUMENT

accommodate the hot body and the lower one of spherical shape added to increase the volume used and also to enclose a standard platinum resistance thermometer. This is needed to measure the temperature of the fluid tested and to calibrate the resistance thermometers placed in the capillary tubes as was discussed on pages 23 through 34 of this paper. On the outer surfaces of the three parts of the cold body are cut the passages for the thermostating fluid. The channels between the different parts are connected by vertical and horizontal bores.

The three parts of the cold body are centered to each other and held together by means of ring nuts. Sealing forces are applied with the aid of screws in the ring nut and act on gold O-rings placed between the parts at proper locations. All surfaces in contact with the test fluid are made of inert material bonded by a special process to the base metal. This material is gold for most of the area but a gold platinum alloy at those locations where sealing forces will be applied and where inertness and mechanical strength are required.

The lower part of the cold body accommodates two valve seats and the vapor pressure measuring device. This device is not used for the valve arrangement shown. The test fluid in this case is in contact with outside instrumentation. For isochoric measurements another valve stem will be inserted which allows the instrument to be evacuated in an open position and is seated so that the vapor pressure measuring device is connected with the test fluid. The pressure transmitter is always at the sample temperature; therefore, pressure changes due to condensation and/or evaporation will not occur.

The upper part accommodates the centering rod and devices for flushing the instrument or to feed-in a well known mass of the sample especially for the determination of p-v-T relations.

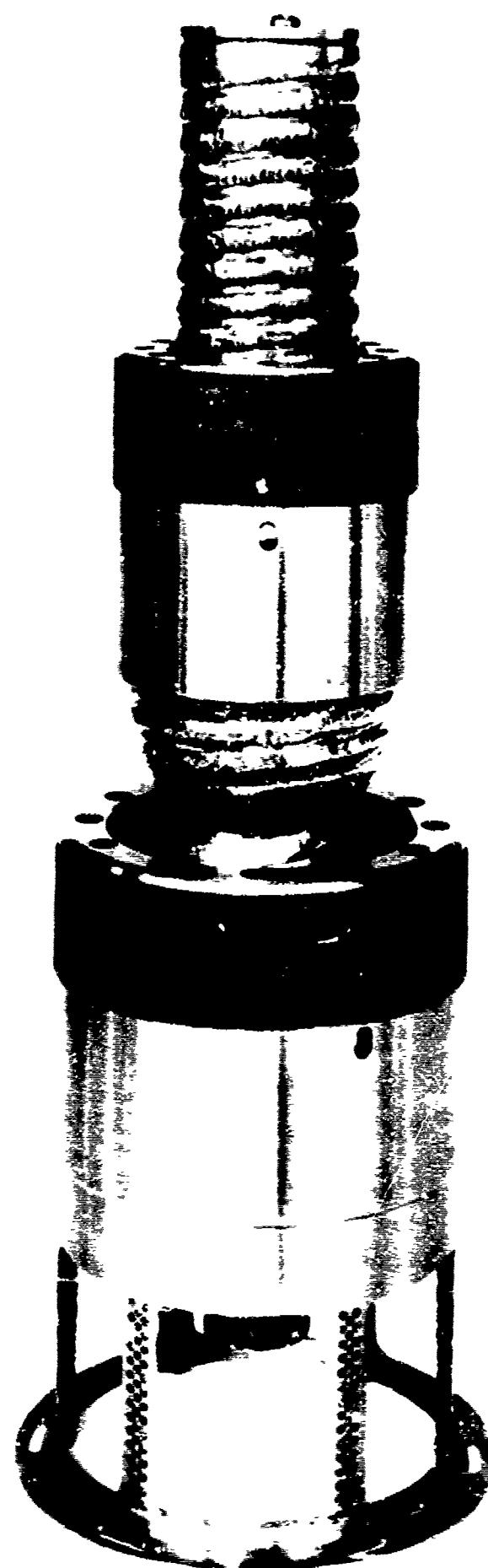


FIGURE 15. MULTI-PURPOSE INSTRUMENT
ASSEMBLED

The hot body, held and centered by the centering rod at its upper end, is centered also at its lower end by means of a centering pin made of pure alumina. Fig. 14 demonstrated also the mounting, insulating and shielding of the instrument.

All the parts of the apparatus have been machined-- the only task remaining is attaching the gold lining. The multi-purpose instrument assembled is shown in Fig. 15.

The design of the major parts and their construction and operation will be discussed in detail in a successive paper. Another paper will deal with the measurements and error analysis of the properties determined.

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ERRATA

Page	Line	
ii	9	Change "materials" to "material".
iia	10	Should read: "... und vom Material des Instrumentes: Wärmeausdehnungskoeffizient und Elastizitätsmodul".
5		add footnote *The following represents the measurements described in [1], and Fig. 2 duplicates Fig. 3 of [1].
7		Table 1 Change "Toulene" to "Toluene".
9		Fig. 3 Change "theoritically" to "theoretically" last line should read: "... the hot body is held by the centering rod....
11	21	Change "a.o." to "etc."
14	6	Change "Ar" to A_r .
	Fig. 5	Change "Time τ_b " to "Time τ ". Change " τ " on abissa to " τ_b ".
	15	Change " $\xi = \zeta$ " to " $\xi = 1$ ".
15	4	Should read: The bulk temperature θ_b of"
19	6	of footnote. Change "assumes" to "assures".
20	Fig. 7	There should be a line connecting automatic control unit with heater. Change Pt-Retistance to Pt-Resistance.
21	31	Change "dampen" to "damp".
22	Fig. 8	Change equation " $T_y = b = T_o + \dots$ " to " $T_{y=b} = T_o + \dots$ ".
24	18	Change "properly" to "property".
29	11	Change "circular section" to "circu. cross-section".
31	17	Change "indicated" to "indicates".
	19	Change "dampens" to "damps".

37 15 Change "choosen" to "chosen".

27 2 Change "aluminumodyd (88%) to
"aluminuoxide (98%)".

44 4 Change "demonstrated" to "demonstrates".

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<p>The development of a new instrument is described and also techniques of measurement to determine; for fluids: 1) thermal conductivity, 2) dielectric constant, and hence 3) index of refraction, 4) electrical conductivity a.c., 5) electrical conductivity d.c.; for gases and vapors: 6) p-v-T properties; for liquids: 7) thermal expansion coefficient, 8) compressibility, 9) vapor pressure, 10) specific heat c, 11) specific heat c; for solids: 12) specific heat; and for instrument materials; thermal expansion coefficient and Young's modulus. A new thermostat operating from about -190°C to 650°C is described. This device is controlled automatically and can follow pre-set temperature-time functions. Detailed analysis is made for the procedure necessary to establish isothermal conditions at surfaces wetted by the test substances and to evaluate deviations from such conditions due to the disturbance of the temperature field in the neighborhood of the surfaces caused by the temperature sensing elements. This also is important so that the correct surface temperature can be derived from the readings of the thermometer. The construction of the centering rod (the most critical part of the multipurpose instrument being a double electrically shielded lead-in and a centering device) is described as is also briefly the final design of the apparatus.</p>		

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Properties over wide ranges of pressure and temperature						
Thermal conductivity						
Dielectric constant						
Index of Refraction						
Electrical conductivity (a.c.)						
Electrical conductivity (d.c.)						
Thermodynamic p-v-T properties (gases and vapors)						
Vapor pressure of liquids						
Compressibility of liquids						
Thermal expansion coefficient of liquids						
Specific heats of liquids						
Specific heat of solids						
Thermostat, calorimeter						
Multi-Purpose instrument						

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